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entitled (64)

**PROCESSES FOR THE PREPARATION OF SOLUBLE
HUMUS-CONTAINING SUBSTANCES.**

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Related Art (56) 115,546(4219/42) 33.1; 31.7.
107,676(3700/38) 31.7; 86.7; 09.2.
12,453/28 31.7.

The following statement is a full description of this invention, including the best method of performing it known

to US

W. G. Murray, Government Printer, Canberra

X377-101-ND-15P.C

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This invention relates to a process for the preparation of substances which resemble naturally-occurring humus, and more particularly, to a process for the preparation of substances useful as cation absorbents and fertilizers.

The substances obtained by the processes of the present invention contain large amounts of a material which possesses chemical properties similar to those of naturally-occurring humus; it is soluble in aqueous alkaline solutions and is in general insoluble in water and aqueous acid solutions.

The term "soluble humus" is used in the specification and claims in reference to the products of the processes of the invention; it refers to that portion which resembles naturally-occurring humus.

So-called soluble humus, comprising humic acid, hymatomelanic acid, fulvic acid, etc., is outstanding for growing plants. Moreover, it has recently been reported that the constituents of soluble humus can be used outside agriculture.

However, manufacture of such substances is very difficult because soluble humus must be very cheap for it to be practical in agriculture, and the composition and chemistry of such substances have not always been made clear.

It has been already proposed to manufacture humic acid by treating a saccharide with a mineral acid at a temperature above about 250°C to yield humine, the said

humine being mixed with caustic soda and oxidised to form
humic acid..

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This process is hazardous and expensive because operations must be carried out at temperatures above 250°C.

Therefore, it is an object of the present invention to provide a new and improved process for the preparation of soluble humus-containing substances.

The present invention relates to a new and improved process for the preparation of soluble humus-containing substances namely by preparing soluble humus directly by reaction of a saccharide and a mineral acid at a temperature lower than about 200°C which is far lower than that of the prior art. The resulting soluble humus-containing substance is useful for the preparation of a fertilizer containing a large amount of soluble humus. Such a fertilizer is extremely useful and effective for growing plants. The present invention provides a process whereby such a fertilizer can be prepared from cheap products such as spent liquor, particularly alcoholic fermentation spent liquor, in general more simply and cheaply, and having better properties, in comparison with conventional fertilizers. In particular, the fermentation spent liquors in general contain various plant nutrients and saccharides which can be incorporated into the fertilizer of the present invention without loss. However it is possible to use materials other than fermentation spent liquors as raw-materials.

According to the present invention, there fore, there is provided a process for the preparation of a soluble humus-containing substance in which an aqueous mixture comprising a saccharide-containing material and a mineral acid, the proportion of acid in the said mixture being 20 to 40% by weight calculated on weight of acid plus water, is heated to a temperature of from 100-200°C, whereby a dehydrated material comprising soluble humus is obtained as a precipitate. The reaction may for example conveniently be effected for a period of 1 to 4 hours. The dehydration is preferably carried out in a closed vessel.

Suitable saccharide-containing materials for use in the process according to the present invention include for example the following:

mono-saccharides, oligosaccharides such as grape sugar, fruit sugar, galactose, pentose, arabinose, sugar canes, starch, starch lees, cellulose, pentosane, waste molasses, fermentation spent liquors, beets, beet pressed pulp, wheats, soybeans, soybean oil lees, rapeseeds, rapeseeds oil lees, and the like.

However, to provide a simple and cheap process, it is advantageous to utilize cheap spent liquors obtained from fermentation works.

Suitable acids in the process according to the invention include phosphoric acid, sulphuric acid, hydro-

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chloric acid and mixtures thereof. The amount of mineral acid depends upon operating conditions, e.g., type of raw material; when sulphuric acid is used, the ratio of saccharide-containing material to sulphuric acid is preferably not greater than about 3:1, but better results can generally be achieved with a ratio of about 1:1.

An excessive amount of mineral acid must be avoided, since it can give rise to increased amounts of insoluble humine, disadvantageously produced from soluble humus by dehydration by the mineral acid.

Referring to the undergoing Table 1, which shows reaction temperatures, it is preferred to carry out.....

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the dehydration of saccharide-containing material with a mineral acid in a closed vessel at a temperature of between 200 - 100°C. Better results can be obtained at 150°C for 1 - 4 hours.

The range covering suitable reaction temperatures can extend considerably when materials containing relatively small amounts of saccharides are utilized. For example, when fermentation spent liquors are utilized, the preferred range of reaction temperatures covers 100 - 150°C.

As far as the utilization of sulphuric acid is concerned, it is preferred to concentrate dilute ^{saccharide} ~~sources~~ ^{and} materials such as waste molasses, fermentation spent liquors to 40 - 50% concentration calculated by weight of solid contents.

The ~~obtained~~ ^{obtained} precipitate is filtered and then is washed with hot water to remove acid radicals such as radicals of sulphuric acid. The precipitate is afterwards dried to obtain a soluble humus-containing substance according to the present invention.

The ~~obtained~~ ^{obtained} precipitate is not soluble in water but at least is partly soluble in alkaline solvent ~~solutions. The portion soluble in alkaline~~ ^{a mineral} ~~The soluble humus in the resultant~~ solution is precipitated by the addition of acids. The precipitate obtained by filtering the said ~~resultant~~ solution shows a golden colour and possesses chemical properties similar to those of natural soluble humus. Furthermore,

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^{it}
~~the acid product~~ possesses a remarkable base exchange
capacity, which ^{is} ~~can be observed~~ as one of the distinguish-
ing features of soluble humus ^{containing} ~~including~~ humic acid from.

other substances.

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Properties of the soluble humus-containing substances according to the present invention can vary according to the variation of operation conditions such as the types of the mineral acid, dehydration temperatures and so on.

The following Table 1 shows the results of various chemical tests including the humus test by Simon's method.

The tests were carried out for a composition resulting from the treatment of 100 parts of grape sugar or glucose with 300 parts of sulfuric acid having a concentration of 20, 30 or 40% at temperatures of 120, 140, 160 and 200°C for 4 hours in a closed vessel.

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TABLE 1

Chemical properties of soluble humus-containing substances
obtained by the treatment of glucose with sulphuric acid:

(1)

(a)	(b)	(c)	(d) humus analysis by Simon's method					(l)
			(e)	(f)	(g)	(h)	(k)	
20	120	56.9	78.9	45.9	21.0	12.0	33.0	43
	140	57.2	79.8	37.0	20.1	23.7	43.8	66
	160	58.9	79.7	38.2	22.7	18.8	41.5	52
	200	61.1	75.1	54.0	13.1	8.0	21.1	41
30	120	61.6	81.2	36.2	12.1	33.0	45.1	97
	140	61.9	83.8	37.2	10.2	36.4	46.6	110
	160	62.3	84.3	37.7	10.0	36.6	46.6	111
	200	64.8	69.5	38.5	15.9	15.1	31.0	41
40	120	60.5	79.9	37.6	17.6	24.7	42.3	79
	140	62.0	80.2	34.7	15.6	29.9	45.5	93
	160	64.1	82.5	36.8	14.6	31.1	45.7	105
	200	65.2	61.1	55.1	--	6.0	6.0	10

Remarks:-

- (a) concentration of sulphuric acid (%)
 (b) reaction temperature (°C)
 (c) carbon in total (%)
 (d) humus analysis by Simon's method (exhausted amount of
 N/10 KMnO_4 in ml per 30 ml of NaF extraction solution)
 (e) soluble humus
 (f) fulvic acid
 (g) rotten substances
 (h) humic acid
 (k) precipitates
 (l) base exchange capacity (m.eq./100 g.)

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(2)

(a)	(b)	(d) humus analysis by Simon's method				
		(e)	(f)	(g)	(h)	(k)
20	120	547.5	165.5	256.5	125.5	382.0
	140	589.9	168.4	286.8	134.7	421.5
	160	648.3	186.5	350.2	131.6	481.8
	200	601.9	159.5	313.3	129.1	442.4
30	120	699.8	178.7	382.6	138.5	521.1
	140	839.5	188.5	398.9	201.1	600.0
	160	788.7	187.6	405.6	195.5	601.1
	200	505.1	160.0	243.9	101.1	345
40	120	659.3	183.7	295.7	179.9	475.6
	140	678.1	184.4	312.9	180.8	493.7
	160	731.9	189.5	352.3	190.1	542.4
	200	472.5	159	216	97.5	313.5

Remarks:-

- (a) concentration of sulphuric acid (%)
- (b) reaction temperature (°C)
- (d) humus analysis by Simon's method (exhausted amount of N/10 KMnO_4 in ml per 30 ml of NaOH extraction solution)
- (e) soluble humus
- (f) fulvic acid
- (g) rotten substances
- (h) humic acid
- (k) precipitates

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In the following Table 2, spent liquor obtained from alcoholic fermentation was treated under various reaction temperatures and period of times to obtain soluble humus-containing substances. In this table, 500 parts of concentrated spent liquor with 40% solid content (200 parts by weight of solid content) was added by a concentrated sulphuric acid (200 parts by H_2SO_4) and was heated to 100, 120, 140, 180, 210 and 250°C respectively for 3 hours in a closed vessel to prepare soluble humus-containing substances.

TABLE 2

Reaction temperature (°C)	Reaction times (hours)	Base exchange capacity (m.eq./100 gr.)
100	1	57
	2	52
	3	57
120	1	59
	2	62
	3	60
140	1	59
	2	62
	3	63
180	3	21
210	3	9.7
250	3	not more than 5

It is shown in the foregoing tables that soluble humus-containing substances obtained by the process according to the present invention possess in general substantially ^{high purity} ~~better yield and higher yield~~ with regard to soluble humus such as humic acid, hymatomelanic acid, fluvic acid and the like and that soluble humus prepared from alcoholic spent liquors at a temperature lower than about 200°C ^{possesses} ~~have~~ in general ^{capacity} ~~large base exchange capacities~~.

Soluble humus-containing substances prepared from alcoholic fermentation spent liquor at a temperature below 140°C possess in general similar base exchange capacities to those of certain minerals such as for example ~~montmorillonites. It is evident therefore~~ ^{montmorillonite group.} ~~These facts can warrant the~~ ^{obtained} ~~conclusion that soluble humus-containing substances~~ ^{by the process} ~~according to the present invention prepared from fermentation~~ spent liquors possess excellent properties as cation absorbents.

Soluble humus-containing substances according to the present invention, which are treated for example with sulphuric acid at temperatures of about 140 - 160°C, possess in general base exchange capacities of more than 100 m. eq./100 g with regard to humine, while base exchange capacities can decrease to less than about 5 m. eq./100 g., when soluble humus-containing substances are prepared at temperatures higher than about 250°C by ~~means of the~~ dehydration with sulphuric acid. It is therefore preferred to carry out the dehydration at a temperature between about 100 - 150°C for fermentation spent liquors. - With regard to the concentration of mineral acid to be utilized, it is preferred to utilize

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a concentration of about 30-40% by weight. The period of time necessary for dehydration may increase as the concentration of the mineral acid decreases. Therefore it is advantageous first to concentrate the spent liquor when dilute liquor is utilized for the preparation of soluble humus-containing substances according to the present invention. It is preferred to concentrate such dilute liquor before the acid is added to about 10-50% by solid content depending on operation conditions including types of raw materials, uses of the product and the like. However, it is not preferred to concentrate the liquor to be utilized up to about 50% solids content, since no additional beneficial results can be obtained from such high concentrations.

It is found that soluble humus-containing substances can be achieved by the dehydration of a saccharide by means of a mineral acid, while various ingredients, which are believed to be effective in growing plants, remain in the product without any remarkable change or diminution and that the mineral acid utilized for the dehydration of saccharides can remain without removal. Such remaining mineral acid and ingredients active in growing plants can be utilized for the preparation of soluble humus-containing fertilizer.

According to a further feature of the present invention, there is provided a process for the preparation of soluble humus-containing fertilizer characterized by the fact that the dehydrated material, especially that obtained

by the dehydration of fermentation spent liquor in particular spent liquor of alcoholic fermentation, is mixed with a suitable material containing phosphoric acid to form a reaction mixture which may then be neutralized by means of a suitable neutralizing agent such as ammonia to form a crude product.

Various minerals and materials useful or necessary in fertilizers, for example potassium compounds, and urea, may be added to the neutralised product, depending upon the desired properties of the end product.

The crude product may then be concentrated and dried to obtain a soluble humus-containing fertilizer according to the present invention.

The detailed construction of the process for the preparation of another soluble humus-containing substance, namely, compound fertilizer containing a large amount of soluble humus, will be described in the following.

Properties of the dehydrated solution obtained from the aforesaid process are exemplified in the following Table 3:

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TABLE 3

(a)	(b)	(c)	(d)	(e)	(f)	(g)
2 : 1	100	1.514	1.161	1.75	20.8	6.24×10^9
	120	1.449	1.147	1.63	22.8	3.24×10^9
	140	1.384	1.170	1.76	23.5	2.21×10^9
1 : 1	100	1.449	1.236	2.31	25.5	3.77×10^9
	120	1.384	1.228	2.10	41.2	2.42×10^9
	140	1.467	1.265	2.43	32.3	4.68×10^9
1 : 2	100	1.508	1.348	3.48	33.8	1.24×10^9
	120	1.419	1.306	2.70	34.6	5.66×10^9
	140	1.569	1.354	3.27	51.0	5.55×10^9

Remarks:

- (a) ratio of concentrated sulphuric acid to solids by weight
- (b) reaction temperature ($^{\circ}\text{C}$)
- (c) density of ^{humine} obtained humine
- (d) density of filtrate
- (e) viscosity of filtrate (c.p.)
- (f) yield of humine (%)
- (g) relative filtration resistance (m/kg)

In the Table 3, a spent liquor of alcoholic fermentation concentrated to 40% ^{mixed with 98%} by solids was ~~added by~~ concentrated sulphuric acid at different ^{weight} ratios in amounts and subjected to dehydration for 3 hours at different temperatures. Viscosities of the ^{resulting} ~~obtained~~ dehydrated ^{materials} ~~solutions~~ are not so high that it is not difficult to ^{process} ~~treat~~ the dehydrated ^{material} ~~solution~~ or ^{the} crude product obtained from the neutralizing

step of this invention.

Spent liquor obtained from alcoholic fermentation works may be first concentrated to about 40-50% by solid. As stated above, higher concentrations up to more than 50% can not give any additional beneficial results. The concentrated liquor is then added by a suitable mineral acid (e.g. sulphuric acid, hydrochloric acid, phosphoric acid; mixture thereof etc.) in the aforesaid amount.

It has been found that the amount of a mineral acid necessary for the dehydration of a saccharide is sufficient for the preparation of the soluble humus-containing fertilizer of this invention. This is because the mineral acid used in the dehydration process is not lost in the first stages. In other words, the amount of mineral acid used in the dehydration step can be determined from the amount necessary to neutralise the material in the subsequent steps after phosphate has been added. Soluble humus-containing fertilizer can be prepared more cheaply by this method in a one-stage process.

The dehydration of a saccharide in spent liquor can be with advantage achieved in a closed vessel in the same manner as described above.

The dehydrated material obtained may then be mixed with a suitable amount of phosphate-containing materials, such as for example apatite, calcium phosphate, calcium biphosphate, superphosphate triple superphosphate and the like. Desirably any suitable material such as potassium

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chloride, potassium sulphate, urea and the like can be added to make up a desired composition in accordance with that of the utilized spent liquor.

It must be noted that spent liquors obtained from alcoholic fermentation works possess in general a considerable amount of potassium content apart from other elements so that it is in general not necessary to add potassium-containing substances to the dehydrated material obtained from the alcoholic fermentation spent liquor.

The soluble humus-containing fertilizer prepared according to the present invention from fermentation spent liquor demonstrated outstanding high efficiency as a compound fertilizer, because it contains not only large amounts of soluble humus including humic acid but also any active ingredients present in the fermentation spent liquor.

It has been found that fertilizers containing more than about 30% of soluble humus according to the present invention are in general much better than conventional fertilizers.

In cultivation tests utilizing the fertilizer according to the undergoing Example 4, it was shown that fertilizer which includes a large amount of soluble humus-containing substances has advantages over conventional fertilizers due to the fact that soluble humus possesses excellent cationic absorption properties.

According to the present invention, it is possible to incorporate more than 50% of soluble humus with other compositions necessary for fertilizer uses.

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If desired, the dehydrated material may be added to conventional fertilizers to improve them. Such improvement can be obtained when at least about 30% of soluble humus-containing substance according to the present invention is mixed with at most about 70% of conventional fertilizer.

However, with regard to costs of preparation and operational hazards, it is far better to utilize the soluble humus-containing fertilizer according to the present invention.

The following non-limitative examples illustrate the invention.

Example 1:

— In a pressure vessel having the glass lining 300 parts of 30% sulphuric acid added to 100 parts of glucose and was heated to 140°C for 3 hours under pressure to obtain a dehydrated material. The resulting dehydrated material containing soluble humus was filtered and washed with hot water to remove sulphuric radicals, afterwards was dried to obtain 64.03 parts of soluble humus-containing substance.

The yields of the obtained product was 83.6% of the theoretical yield, which was calculated by an assumption that 10 mols of water is dehydrated from 4 mols of glucose.

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Table 4 shows the results obtained from various chemical tests including the humus analysis by Simon's method (exhausted amount of N/10 KMnO_4 in ml per 30 ml of NaF or NaOH extraction solution).

TABLE 4

Simon's method	Extraction with	
	NaF	NaOH.
soluble humus	79	840
fulvic acid	52	399
rotten substances	4	369
humic acid	23	374
precipitates	27	741
degree of formation of humus	85.2	50.5
<hr/>		
carbon in total (%)	59.9	
base exchange capacity	89	
(m.eq./100g.)		

Example 2:

A mixture of 100 parts of glucose with 300 parts of 30% phosphoric acid was treated in an analogous manner to that of Example 1 with the exception of a dehydration temperature of 160°C to obtain 59.4 parts of a soluble humus-containing substance.

The following Table 5 shows various chemical properties of the obtained product (by Simon's method: exhausted amount of KMnO_4 in ml per 30 ml of NaF or NaOH extraction).

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TABLE 5

<u>Simon's method</u>	Extraction with	
	NaF	NaOH
soluble humus	83.8	678.1
fulvic acid	37.2	184.4
rotten substances	10.2	312.9
humic acid	36.4	180.8
precipitates	46.6	497.3
degree of formation of humus	78	37

carbon in total (%)	61.9
base exchange capacity (m.eq./100g.)	110

Example 3:

In an analogous manner to that of Example 1,
100 parts of soybean oil lees having the following composition ^{was} ~~was~~ treated with 300 parts of 30% sulphuric acid at 140°C for 5 hours to obtain 44.5 parts of a soluble humus-containing substance.

water	11.13%
nitrogen in total	6.76%
crude protein	42.25%
direct reducing saccharides	trace
saccharides in total	20.91%

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The following Table 6 shows the results obtained from various chemical tests including humus tests by Simon's method:

TABLE 6

Simon's method	Extraction with	
	NaF	NaOH
soluble humus	171	6450
fulvic acid	159	450
rotten substances	4	5941.5
humic acid	9	58.5
precipitates	13	6000
degree of formation of humus	69.2	0.97
<hr/>		
carbon in total (%)		52.19 521.9
base exchange capacity (M.eq./100g.)		34

Example 4:

Spent liquor obtained from alcoholic fermentation utilizing molasses having the following compositions was concentrated to 40% solids:

solids in weight	7.0%
saccharides in total	11.5%
nitrogen in total	1.8%
phosphoric acid in total	0.4%
potassium in total	12 %
ash in total	26 %

1,425 kg of the said concentrated spent liquor
(solids in total -- 570 kg) was added by 266 kg of

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98% sulphuric acid and was heated to 120°C for 2 hours to obtain a soluble humus-containing substance. The said substance was mixed with 131 kg of 40% in weight of triple superphosphate to obtain a mixture.

The said mixture was neutralized with 90.75 kg of aqueous ammonia and dried over by ^{heating} ~~the distillation~~ to obtain 1,000 kg of a soluble humus-containing fertilizer having the effective composition shown in Table 7.

^A ~~According to this example, a fertilizer having~~ a well balanced composition shown in the undergoing Table 7 can be prepared without any further addition of elemental compositions. ^{The reason is that} ~~It is true since that spent~~ liquors obtained from alcoholic fermentation works include in general various ^{effective} ~~effective~~ compositions for fertilizer uses.

TABLE 7

Total nitrogen	8.53%
ammonia nitrogen	7.01%
Total phosphoric acid	5.63%
W-P ₂ O ₅ (water soluble phosphoric acid)	4.78%
W-K ₂ O Water soluble potassium	6.84%
Water	2.0 %
pH	4.5

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Example 5:

Spent liquor of lysine fermentation having the following compositions was concentrated to 40% solids:

solids in weight	6.26%
saccharides in total	12.1 %
nitrogen in total	7.91%
ammonia nitrogen	5.07%
phosphoric acid in total	0.50%

potassium in total 5.42%

— 108 kg of 98% sulphuric acid was added to 11,440 kg of the said concentrated spent liquor

(solids in total - 576 kg) ~~was added by 103 kg of 93%~~

~~sulphuric acid~~ and was heated to 120°C for 8 hours to

obtain a soluble humus containing solution. To this

solution there were added 238.5 kg of 35% triple super-

phosphate and 87.6 kg of potassium sulphate to form a

mixture. The said mixture was then neutralized with

36.4 kg of aqueous ammonia and dried over by ^{heating} ~~distillation~~

to obtain 1,000 kg of soluble humus-containing fertilizer

by having the effective composition shown in Table 8.

The following Table 8 shows the result obtained from chemical analysis of this product:

TABLE 8

Total nitrogen	7.56%
ammonia nitrogen	5.61%
Total phosphoric acid	8.75%
Water soluble phosphoric acid.	6.58%
Water soluble potassium	7.46%
Water	2.0 %
pH	4.5

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A process for the preparation of a soluble humus-containing substance in which an aqueous mixture comprising a saccharide-containing material and a mineral acid, the proportion of acid in the said mixture being 20 to 40% by weight (calculated on the weight of acid plus water), is heated to a temperature of from 100-200°C whereby a dehydrated material comprising soluble humus is obtained as a precipitate.
2. A process as claimed in claim 1 in which said saccharide-containing material is a mono-, di, tri- or tetra-saccharide, sugar cane, starch, starch lees, cellulose, pentosan, waste mollasses, fermentation spent liquor, beet, beet pressed pulp, wheat, soybean, soybean oil lees, rapeseed, or rapeseed oil lees.
3. A process as claimed in claim 2 in which said mono-saccharide-containing material is grape sugar (glucose), fruit sugar fructose), galactose, pentose, or arabinose.
4. A process as claimed in claim 2 in which said saccharide-containing material is alcoholic fermentation spent liquor.
5. A process as claimed in any of the preceding claims in which the said mineral acid is sulphuric acid, hydrochloric acid, phosphoric acid, or a mixture of at least two thereof.
6. A process as claimed in claim 5 in which the acid is sulphuric acid and the ratio of saccharide-containing

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material to sulphuric acid is not greater than 3:1.

7. A process as claimed in claim 6 in which said ratio is 1:1.

8. A process as claimed in any of the preceding claims in which, where the saccharide-containing material is a fermentation spent liquor, the dehydration is effected at 100-150°C.

9. A process as claimed in any of the preceding claims in which a dilute aqueous solution of saccharide-containing material is previously concentrated at 10 to 50% solids by weight.

10. A process as claimed in claim 9 in which where the mineral acid is sulphuric acid, a dilute saccharide-containing source is previously concentrated at 40-50% solids by weight.

11. A process as claimed in claim 10 in which said dilute saccharide-containing source is waste molasses or fermentation spent liquor.

12. A process as claimed in any of the preceding claims in which the dehydration is effected in a closed vessel.

13. A process as claimed in any of claims 1 to 11 whereafter a phosphate-containing material is added to the said dehydrated material.

14. A process as claimed in claim 13 in which the phosphate-containing material is apatite, calcium phosphate, calcium biphosphate, calcium superphosphate, or triple superphosphate, or a mixture of two or more thereof.

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15. A process as claimed in claim 13 or claim 14 in which potassium chloride, potassium sulphate, and/or urea, is added to the said solution.
 16. A process as claimed in any of claims 13 to 15 whereafter the mixture is neutralised.
 17. A process as claimed in claim 16 in which the neutralising agent is ammonia.
 18. A process as claimed in any of claims 13 to 17 whereafter the mixture is dried.
 19. A process as claimed in any of the preceding claims substantially as herein described.
 20. A process as claimed in any of the preceding claims substantially as herein described in any of the Examples.
 21. A soluble humus-containing fertilizer whenever prepared by a process as claimed in any of the preceding claims.
 22. A fertilizer as claimed in claim 21 containing more than 50% by weight of soluble humus.
 23. A cation absorbent whenever prepared by a process as claimed in any of claims 1 to 12.
- DATED this 13th day of December, 1971.
- KYOWA HAKKO KOGYO K.K.